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SUFFIELD REPORT

NO. 412

THE IDENTIFICATION OF COMPOUNDS IN MUSTARD HYDROLYSATE (U)

by

P.A. D'Agostino and L.R. Provost

PCN No. 13E20

April 1985

DEFENCE RESEARCH ESTABLISHMENT SUFFIELD, RALSTON, ALBERTA

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ABSTRACT

About 700 tons of World War II mustard stored at the Defence Research Establishment Suffield was destroyed by hydrolysis during the 1970's. Samples of the liquid and sludge layers of the hydrolysate were retained and have now been analysed by gas chromatography using flame ionization and mass spectral detection. Hydrolysis was essentially complete since only trace levels of unreacted mustard were detected. Thiodiglycol, a hydrolysis product of mustard, was the major component identified in the hydrolysate. A number of other compounds were identified (or tentatively identified) in both the liquid and sludge hydrolysate samples.

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TABLE OF CONTENTS

Page No.

ABSTRACT

ACKNOWLEDGEMENTS

TABLE OF CONTENTS

INTRODUCTION 1

EXPERIMENTAL 3

Hydrolysate Samples 3

Instrumental Analysis 3

RESULTS AND DISCUSSION 3

Determination of Mustard and Thiodiglycol 3

Identification of other Hydrolysate Compounds 4

Aqueous Hydrolysate 5

Chloroform Extracts of the Hydrolysate 6

CONCLUSIONS 8

REFERENCES 9

TABLES

FIGURES

APPENDIX

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INTRODUCTION

1. During World War II over 700 tons of the chemical warfare agent mustard were shipped to the Defence Research Establishment Suffield (DRES) and stored in five lead-lined concrete vaults (1). In the early 1970's research was begun to find a safe, efficient, economical and environmentally acceptable method of destroying the DRES mustard. Laboratory studies indicated the feasibility of using batch hydrolysis provided the ratio of water to mustard was large, the temperature was elevated to 100°C and the pH was maintained above 7 (2). The mustard was hydrolysed in 1000 gallon batches using 5000 pounds of lime ($Ca(OH)_2$) and 2500 gallons of water (2, 3).

2. The principle reactions involved in the hydrolysis of mustard (H) are shown in the equations below (4). Conversion of mustard $\underset{\sim}{1}$ through hemisulfur mustard $\underset{\sim}{2}$ to thiodiglycol $\underset{\sim}{3}$ was reported to be essentially complete under the conditions adopted at DRES (2). A recent analysis of the hydrolysate at DRES indicated the presence of large amounts of the decomposition product thiodiglycol and trace levels of mustard (5).

$$\underset{\underset{\sim}{1}}{Cl\text{-}CH_2\text{-}CH_2\text{-}S\text{-}CH_2\text{-}CH_2\text{-}Cl} + H_20 \rightarrow \underset{\underset{\sim}{2}}{HO\text{-}CH_2\text{-}CH_2\text{-}S\text{-}CH_2\text{-}CH_2\text{-}Cl} + HCl$$

$$\underset{\underset{\sim}{2}}{HO\text{-}CH_2\text{-}CH_2\text{-}S\text{-}CH_2\text{-}CH_2\text{-}Cl} + H_20 \rightarrow \underset{\underset{\sim}{3}}{H0\text{-}CH_2\text{-}CH_2\text{-}S\text{-}CH_2\text{-}CH_2\text{-}OH} + HCl$$

$$Ca(OH)_2 + 2\,HCl \rightarrow Ca(Cl)_2 + 2\,H_20$$

3. The mustard hydrolysate was transferred from the reaction vessel into one of five empty storage vaults following hydrolysis. After a cooling and settling period the hydrolysate separated into two layers. The upper (liquid) layer was very fluid and ranged from colourless to pale yellow in colour. Samples from the lower (sludge) layer were paste-like and yellow-brown in colour. A sample of the liquid and sludge layer from each vault was retained for this analysis.

4. The objectives of this study were: a) to confirm the presence of thiodiglycol and mustard, b) to identify, where possible, other components in both the liquid and sludge hydrolysate samples, and c) to provide information that will aid in the identification of mustard decomposition products in environmental samples. Chloroform extracts of the liquid and sludge samples, were screened for the presence of mustard and other compounds by packed column gas chromatography with flame ionization detection (GC-FID). The liquid layer samples and water extracts of the sludge layer samples were analysed similarly for thiodiglycol and other hydrolysate products. Thiodiglycol, mustard and a number of other compounds were identified in the hydrolysate samples by combined gas chromatography-mass spectrometry (GC-MS).

EXPERIMENTAL

Hydrolysate Samples

6. Samples of the liquid and sludge hydrolysate layers were stored in polyethylene bottles. Figure 1 illustrates the analytical scheme followed during analysis of the samples. The method was described in detail in a prior publication (5).

Instrumental Analysis

7. A Varian 3700 (Varian Associates, Georgetown, Ont.) gas chromatograph was used for packed column GC-FID and GC-MS analyses. Packed column GC-MS analyses were performed using a VG-Micromass 70/70H double-focusing mass spectrometer (VG Analytical, Wythenshaw, UK) in the electron-impact mode. Operating condition for packed column GC-FID and GC-MS are presented in Tables I and II respectively.

RESULTS AND DISCUSSION

8. Both mustard and thiodiglycol were quantitated in the DRES mustard hydrolysate samples. A number of compounds were identified (or tentatively identified) based on the mass spectral and gas chromatographic data obtained during this study. In addition, a semi-quantitative estimate of concentration was made for the major components found in both the liquid and sludge hydrolysate.

Determination of Mustard and Thiodiglycol

9. Trace levels of mustard were detected in the chloroform extracts of the sludge from vaults 6 and 8. Mustard was confirmed by packed column GC-MS in the selected-ion-monitoring mode at 2.9 and 4.2 $\mu g/g$ of sludge in these two vaults respectively (5). No mustard was detected in the chloroform extracts of the liquid hydrolysate.

10. Thiodiglycol was quantitated by packed column GC-FID using external standard calibration and confirmed by GC-MS. It was found in the 6.2 to 13.9 mg/g range in the water extracts of the sludge and in the 2.2 to 10.3 mg/mL range in the neat liquid hydrolysate (5). Table III summarizes this data.

Identification of other Hydrolysate Compounds

11. Packed column GC-MS was used to obtain electron-impact mass spectra for the major components isolated in the aqueous and chloroform extracts of the hydrolysate samples. A mass spectral and GC retention time match with standards was used for identification purposes. A number of compounds were identified in the hydrolysate using this method. Tentative identification of some of the other compounds was possible on the basis of mass spectral match alone.

12. Fundamental interpretation of the mass spectral data was required where a match was not found in the DRES or other mass spectral data bases (6, 7). Possible molecular formulas and in some cases plausible structures were advanced based on the acquired data. The molecular ion isotope ratio and characteristic fragmentation ions were most useful in the interpretation of the mass spectra of the compounds isolated from the hydrolysate.

13. It was possible to estimate the number of sulfur atoms in an unknown using molecular ion information since the ^{34}S isotope occurs naturally at 4.39%. The molecular ion ratio, $M^{\cdot+}$ to $(M+2)^{\cdot+}$, of known components in the hydrolysate was compared to the theoretical value calculated based on the natural occurrence of ^{32}S and ^{34}S. The ratio data for a large number of the hydrolysate components is presented in Tables IV and V. The experimental $M^{\cdot+}$ to $(M+2)^{\cdot+}$ ratio was always higher than theoretically expected. This is probably due to background noise contributions which are more significant for the less intense $(M+2)^{\cdot+}$ ion than for the $M^{\cdot+}$ ion.

14. Experimental $M^{\cdot+}$ to $(M+2)^{\cdot+}$ ratios of approximately 100:7, 100:12 and 100:19 were determined for compounds known to contain one, two and three sulfur atoms respectively. This compares to theoretical values of about 100:5, 100:9 and 100:13. Enhancement of the $(M+2)^{\cdot+}$ ion due to carbon and oxygen presence were taken into account for all calculations. Computer generated formulas were limited to compounds containing carbon, hydrogen, oxygen and sulfur. Possible molecular formulas for hydrolysate unknowns with measureable $M^{\cdot+}$ to $(M+2)^{\cdot+}$ ratios are listed in Tables IV and V.

15. Compounds containing chlorine were easily identified based on the characteristic molecular ion cluster associated with the occurrence of ^{35}Cl and ^{37}Cl. Possible molecular formulas, based on the presence of two chlorine atoms, are presented in Table III for an unknown compound found in the chloroform extract of the sludge hydrolysate.

16. The presence of sulfur in these compounds was substantiated by several charactertistic low mass fragmentation ions. Fragmentation ions at m/z 59, m/z 60 and m/z 61 were found to be characteristic of this group of sulfur containing compounds. These ions were observed repeatedly throughout the study and probably correspond to $(S - CH = CH_2)^+$, $(S - CH_2CH_2)^{+\cdot}$ and $(H - S - CH_2CH_2)^+$ respectively. One or more of these ions was evident in all the mass spectra illustrated in Figures 3, 4 and 5 and tabulated in Appendix 1. The m/z 45, $(CH - S)^+$, and m/z 46, $(CH_2 - S)^{+\cdot}$ fragmentation ions are also characteristic of these compounds. Figure 3 illustrates the presence of these ions in five compounds isolated from the liquid hydrolysate and the water extracts of the sludge samples. The m/z 64 fragmentation ion, due primarily to $(S - S)^{+\cdot}$, suggests that the unknown contains a minimum of two sulfur atoms. Significant m/z 64 ions are evident in Figures 3, 4 and 5 for compounds containing two or more sulfur atoms.

17. Appendix 1 contains the mass spectral data for all the compounds not represented in Figures 3, 4 and 5. This data was included since identification of unknowns may be possible in the future with the availability of new standards or further research.

Aqueous Hydrolysate

18. Five compounds, including thiodiglycol, were identified in the neat liquid hydrolysate and the water extracts of the sludge samples. Figure 2 illustrates two chromatograms obtained during packed column GC-FID analysis. 1,4-Thioxane, 1,4-dithiane, hemisulfur mustard and thiodiglycol were identified in one or more of the samples studied. Identifications were based on a mass spectral and GC retention time match with a standard. Figure 3 illustrates the electron-impact mass spectra obtained for these compounds. Published mass spectra (6, 7) were similar to those obtained for 1,4-thioxane, 1,4-dithiane and thiodiglycol.

19. The mass spectrum illustrated in Figure 3(b) was not similar to any alkyl-thiol ($C_5H_{12}S$), oxathiolane or oxathiane published (6, 7). Fundamental interpretation of the mass spectral data suggested that it could be (2-vinylthio)ethanol. This compound could be formed by the dehydration of thiodiglycol. Dehydration may be possible under acidic conditions at elevated temperatures. pH values of less than 7 were noted for the liquid hydrolate samples provided.

20. Table III summarizes the amounts of each major component in the neat liquid hydrolysate and the water extracts of the sludge samples. Thiodiglycol was quantitated by packed column GC-FID (in triplicate) using the external standard calibration method. A semi-quantitative estimate was made for the other compounds based on the FID peak height response of thiodiglycol. This was considered sufficient for these compounds since the emphasis was placed on qualitative identification.

Chloroform Extracts of the Hydrolysate

21. A large number of compounds were observed during the gas chromatographic study of the chloroform extracts of the liquid and sludge hydrolysate. Figures 6 and 7 illustrate the packed column GC chromatograms obtained during analysis of the sludge and liquid samples respectively. Many compounds were identified on the basis of their mass spectra and gas chromatographic data. Tentative identification of several compounds was possible by comparison of the mass spectrum with library (6, 7) or literature spectra. As is often the case in broad spectrum analysis, a number of compounds remain unidentified. Possible molecular formulas, based on their mass spectral data, are presented for these unknowns in Tables IV and V.

22. Twenty-five major components were identified in the chloroform extracts of the sludge hydrolysate samples. 1,4-Thioxane, 1,4-dithiane and 1,2,5-trithiapane were positively identified using the DRES data base. The mass spectra of these compounds are illustrated in Figures 3(a), 3(c) and 4(e) respectively. The mass spectrum of 1,2,5-trithiapane obtained was similar to that in the literature (8). Two other ring structures, 2-methyl-1,3-oxathiolane (Figure 2(a)) and 1-oxa-4,5-dithiacycloheptane (Appendix 1 – 16) were tentatively identified using mass spectral data published in references (6) and (9) respectively.

23. The mass spectrum of the unknown illustrated in Figure 4(b) suggests that this compound may be similar in structure to 2-methyl-1,3-oxathiolane (Figure 4(a)). Both compounds show significant $(M\text{-}CH_3)^+$ fragmentation ions. The presence of an intense m/z 64, $(S_2)^{\cdot+}$, ion and a $M^{\cdot+}$ to $(M+2)^{\cdot+}$ ratio of 100:9 suggest a compound containing two sulfur atoms. This component probably only differs from 2-methyl-1,3-oxathiolane by the replacement of an oxygen with a sulfur atom. Thus the unknown in Figure 4(b) is probably a methyl substituted 1,3-dithiolane.

24. Both bis(2-chloroethyl)disulfide and bis(2-chloroethyl)trisulfide were identified using mass spectral and gas chromatographic data. The presence of these polysulfides is consistent with an earlier study (10) which indicated that Levenstein mustard (undistilled mustard) contained approximately 30% by weight unhydrolysable material (namely polysulfides and elemental sulfur). Figures 5(a) and 5(b) illustrate the mass spectral data acquired for these polysulfides. An additional compound containing two chlorine atoms remains unidentified. Possible molecular formulas for this compound (Figure 5(e)) are presented in Table IV.

25. The mass spectra of several compounds that remain unknown are presented in Figures 4(c), 4(d), 5(b) and 5(d). Possible molecular formulas and fragmentation ions based on their mass spectral data are presented in these figures. The compounds in Figures 4(c) and 4(d) appear to differ only in the replacement of an oxygen with a sulfur atom since their fragmentation pattern is similar.

26. Table IV lists the compounds and possible molecular formulas of unknowns identified in the sludge sample extracts. A semi-quantitative estimate of concentration was made based on the FID response of mustard. The major components account for 0.1 to 3.6% of the total weight of the sludge. It is interesting to note that the two sludge samples with the highest organic content, namely vaults 6 and 8, contained the only detectable traces of mustard.

27. Fourteen compounds were isolated during GC analysis of the chloroform extracts of the liquid samples. Tentative molecular formulas were advanced based on mass spectral evidence. The molecular formulas and an estimate of concentration, also based on the FID response of mustard, are presented in Table V.

28. Most of the compounds were of higher molecular weight and identification of a molecular ion was often difficult. Since these compounds were water soluble it is possible that some of the data accumulated may be due to the thermal degradation products of sulfonium salts. These salts have been isolated during the hydrolysis of mustard (4).

29. The organic content was less in the chloroform extracts of the liquid hydrolysate. Organic content, based on the major components identified in the liquid hydrolysis, was less than 0.1% for all the samples studied.

CONCLUSIONS

30. The hydrolysis of all the mustard destroyed at DRES was essentially complete since only trace levels of mustard were detected in two of the sample extracts. Thiodiglycol, the principle hydrolysis product of mustard, was found to be the major organic component in the aqueous sample.

31. A number of other components were identified in the hydrolysate samples based on their mass spectral and gas chromatographic data. Tentative identification was possible for several compounds based on comparison of their mass spectral data with published spectra. Mass spectral interpretation led to the assignment of possible molecular formulas for several unknown components.

32. As is often the case in broad spectrum analysis, some compounds remain as unknowns. The mass spectral data for these compounds are included to aid in possible future identification.

33. It could not be determined from these samples whether many of the compounds observed in the hydrolysate were present in the original mustard or were hydrolysis products. However, since hydrolysis represents a major chemical decomposition pathway, it would be possible to suggest the prior presence of mustard in environmental samples based on the identification of thiodiglycol and other hydrolysate components.

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TABLE I

PACKED COLUMN GC-FID CONDITIONS

	AQUEOUS[1] SAMPLES	CHLOROFORM[2] SAMPLES
GC COLUMN:	1.22 m × 1.5 mm i.d. Tenax GC, 60/80 mesh (Alltech Assoc., Arlington, IL)	1.22 × 1.5 m i.d. 5% OV 101 on 80/100 mesh Chromosorb W (Chromatographic Specialies Ltd., Brockville, Ont)
TEMPERATURE PROGRAM:	150° for 1 min, then 10°/min to 250°C and held for 5 min	50° for 2 min, then 5°/min to 250°C and held for 10 min
INJECTION TEMPERATURE:	250°C	250°C
CARRIER GAS:	High purity helium[3,5] at 20 mL/min	High purity helium[3,5] at 25 mL/min
FID GASES:	Zero air[4,5] at 300 mL/min, ultra high purity hydrogen[4,5] at 30 mL/min	
FID TEMPERATURE:	250°C	

1 Liquid layer samples and aqueous extraction of sludge layer samples.

2 Chloroform extracts of both the liquid and sludge layer samples.

3 Helium is passed through Drierite, molecular sieve, dust and oxygen removal filters.

4 Air and hydrogen are passed through Drierite, molecular sieve and dust filters.

5 Gas supplier: Liquid Carbonic Canada Ltd. (Scarborough, Ontario).

TABLE II

PACKED COLUMN GC-MS CONDITIONS

OPERATING PARAMETERS	AQUEOUS[1] SAMPLES	CHLOROFORM[2] SAMPLES
GC COLUMN:	1.22 m × 1.5 mm i.d. Tenax GC, 60/80 mesh	1.83 × 1.5 mm i.d. OV 101 on 80/100 Chromosorb W
GC-MS INTERFACE:	Jet Separator (230°C)	
IONIZATION MODE:	Electron Impact	
ELECTRON ENERGY:	70 eV	
EMISSION:	200 μA	
SOURCE TEMPERATURE:	190 – 200°C	
SOURCE PRESSURE:	ca. 2×10^{-6} torr	
SCAN FUNCTION AND RATE:	**Scanning:** 350 to 20 amu, exponential down scan, 3 sec/decade **SIM:** m/z 100 (PFK lock mass), 109, 111, 158 and 160 with 200 kmsec/ion dwell time (Mustard Determination)	
ACCELERATING VOLTAGE:	**Scanning:** 4 kV **SIM:** stepped from 4 kV downwards	
RESOLUTION (10% VALLEY DEFINITION):	**Scanning:** 500 **SIM:** 200 to 300	

1 Liquid layer samples and aqueous extraction of sludge layer samples.

2 Chloroform extracts of both the liquid and sludge layer samples.

Table III

COMPOUNDS IDENTIFIED IN LIQUID HYDROLYSATE AND WATER EXTRACTS OF SLUDGE HYDROLYSATE

CHROMATOGRAM PEAK NUMBER[a]	COMPOUND IDENTIFIED	MOL. WT.	VAULT CONCENTRATION										MASS SPECTRAL DATA
			6		7		8		9		10		
			mg/mL[b]	mg/g[c]	mg/mL[b]	mg/g[c]	mg/mL[b]	mg/g[c]	mg/mL[b]	mg/g[c]	mg/mL[b]	mg/g[c]	
1	1,4-Thioxane	104	1.4	1.5	0.84	2.2	0.56	0.66	2.5	1.9	1.9	1.8	Figure 3a
2	(2-Vinylthio)ethanol[d] $CH_2 = CH$ $HO - CH_2 - CH_2$ S	104	—	1.7	0.74	2.6	—	0.66	—	—	—	—	Figure 3b
3	1,4-Dithiane	120	1.3	1.4	0.59	3.1	0.56	0.31	1.9	2.5	1.3	1.3	Figure 3c
4	Hemisulfur mustard $HO - CH_2CH_2$ S $Cl - CH_2CH_2$	140	—	—	—	—	—	—	1.9	3.1	—	0.66	Figure 3d
5	Thiodiglycol $HO - CH_2CH_2$ S $HO - CH_2CH_2$	122	4.7 ± .1	11.8 ± .9	4.4 ± .2	7.7 ± .5	2.2 ± .1	6.2 ± .3	10.3 ± .5	13.9 ± .3	6.1 ± .4	12.0 ± .5	Figure 3e
% Organic Content in Sample			0.7%	1.6%	0.7%	1.6%	0.3%	0.8%	1.7%	2.1%	0.9%	1.6%	

[a] Refer to Figure 2.

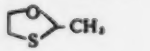
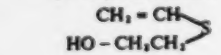
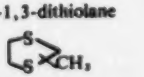
[b] mg/mL of liquid hydrolysate.

[c] mg/g of sludge hydrolysate.

[d] Tentative identification based on mass spectral interpretation.

Table IV

MAJOR COMPONENTS IDENTIFIED IN THE CHLOROFORM EXTRACTS OF THE SLUDGE HYDROLYSATE

CHROMATOGRAM PEAK NUMBER[a]	COMPOUND IDENTIFIED (or tentatively identified)	MOL.[b] WT.	VAULT CONCENTRATION (mg/g of Sludge)[c]					M:M+2 RATIO		NUMBER OF SULFUR ATOMS[d]	MASS SPECTRAL DATA
			6	7	8	9	10	EXPERIMENTAL	THEORETICAL		
1	2-Methyl-1,3-oxathiolane 	104	2.8	—	3.4	—	—	100:6.9	100:4.7	1	Figure 4a
1	1,4-Thioxane	104	0.94	0.07	0.87	0.34	0.02	100:7.1	100:4.7	1	Figure 3a
3	(2-Vinylthio)ethanol 	104	0.62	0.32	0.22	—	—	100:6.1	100:4.7	1	Figure 3b
4	Methyl-1,3-dithiolane 	120	2.4	0.27	2.6	0.40	0.03	100:10	100:8.9	2	Figure 4b
5	1,4-Dithiane	120	1.0	—	1.5	0.30	—	100:10	100:8.9	2	Figure 3c
6	*$C_3H_6S_2O$ $C_4H_8SO_2$	124	3.4	0.92	3.7	1.5	0.14	100:14	100:9.0 100:4.8	2	Figure 4c
7	$C_7H_{16}SO$ $C_6H_{12}SO_2$ $C_6H_{12}S_3$	148	0.28	0.04	0.31	—	—	m/z 150 not detected	—	—	Appendix 1-15

.../2

Table IV (Cont'd)

CHROMATOGRAM PEAK NUMBER[a]	COMPOUND IDENTIFIED (or tentatively identified)	MOL.[b] WT.	VAULT CONCENTRATION (mg/g of Sludge)[c]					M:M+2 RATIO		NUMBER OF SULFUR ATOMS[d]	MASS SPECTRAL DATA
			6	7	8	9	10	EXPERIMENTAL	THEORETICAL		
8	1-Oxa-4,5-dithiacycloheptane	136	0.06	0.02	0.12	—	—	100:14	100:9.1	2	Appendix 1-16
9	Unknown	140	0.24	0.09	0.27	0.27	—	m/z 142 not detected	—	—	Appendix 1-17
10	*$C_4H_{10}S_2O$ $C_4H_{10}SO_2$	138	1.4	0.49	0.93	0.94	0.11	100:13	100:9.1 100:5.1	2	Appendix 1-3
11	*$C_3H_6S_3O$ $C_3H_6S_3O_2$	156	0.82	0.23	1.1	0.34	—	100:19	100:13 100:9.4	3	Figure 4d
12	1,2,5-Trithiapane	152	1.6	0.39	2.0	0.67	0.05	100:19	100:13	3	Figure 4e
13	bis(2-Chloroethyl)disulfide $Cl\text{-}CH_2CH_2\text{-}S_2\text{-}CH_2CH_2\text{-}Cl$	192	1.5	—	2.4	—	—	—	—	—	Figure 5a
14	*$C_7H_{16}S_2$ *$C_6H_{12}S_2O$ $C_7H_{16}SO_2$ $C_6H_{12}SO_2$	164	2.6	1.1	—	—	—	100:16	100:9.1 100:9.2 100:5.1 100:5.2	2	Appendix 1-6

.../3

Table IV (Cont'd)

CHROMATOGRAM PEAK NUMBER[a]	COMPOUND IDENTIFIED (or tentatively identified)	MOL.[b] WT.	VAULT CONCENTRATION (mg/g of Sludge)[c]					M:M+2 RATIO		NUMBER OF SULFUR ATOMS[d]	MASS SPECTRAL DATA
			6	7	8	9	10	EXPERIMENTAL	THEORETICAL		
15	*$C_8H_{12}S_3$ *$C_4H_6S_3O$ $C_8H_{12}S_2O_2$ $C_4H_6S_2O_2$	168	—	—	1.9	—	—	100:23	100:13 100:13 100:9.3 100:9.5	3	Figure 5b
16	Unknown	172	0.63	0.07	0.87	0.13	—	m/z 174 not detected	—	—	Appendix 1-18
17	Unknown	152	—	0.25	—	—	—	m/z 154 not detected	—	—	Appendix 1-19
18	*$C_8H_{14}S_3$ $C_8H_{14}SO_3$ $C_9H_{16}SO$	174	1.3	0.22	1.4	0.94	—	100:12	100:9.2 100:5.2 100:5.1	2	Appendix 1-20
19	bis(2-Chloroethyl) trisulfide $Cl\text{-}CH_2CH_2\text{-}S_3\text{-}CH_2CH_2\text{-}Cl$	222	5.4	—	7.3	1.9	—	—	—	—	Figure 5c
20	*$C_4H_6S_4$ $C_4H_6S_3O_2$ $C_8H_{12}S_2$ $C_4H_6S_2O_4$	184	2.4	0.28	2.6	0.88	0.09	100:33	100:18 100:14 100:14 100:9.7	4	Figure 5d
21	Unknown	—	—	—	1.9	—	—	—	—	—	Appendix 1-21

.../4

Table IV (Cont'd)

CHROMATOGRAM PEAK NUMBER[a]	COMPOUND IDENTIFIED (or tentatively identified)	MOL.[b] WT.	VAULT CONCENTRATION (mg/g of Sludge)[c]					M:M+2 RATIO		NUMBER OF SULFUR ATOMS[d]	MASS SPECTRAL DATA
			6	7	8	9	10	EXPERIMENTAL	THEORETICAL		
22	*$C_8H_{14}S_3$ $C_8H_{14}S_2O_2$ $C_9H_{16}S_2O$ $C_{10}H_{22}S_2$	206	2.9	0.95	1.6	0.54	—	100:24	100:14 100:9.6 100:9.5 100:9.4	3	Appendix 1-22
23	*$C_8H_{16}S_3$ $C_8H_{16}S_2O_2$ $C_9H_{16}S_2O$	208	—	0.28	—	0.67	0.07	100:24	100:14 100:9.6 100:9.5	3	Appendix 1-23
24	$C_8H_{16}S_3$ $C_8H_{16}S_2O_2$ $C_9H_{10}S_2O_2$	208	—	0.07	0.30	—	—	100:24	100:14 100:9.6 100:9.5	3	Appendix 1-24
25	$C_9H_{20}SOCl_2$ $C_8H_{16}SO_2Cl_2$ $C_7H_{12}SO_2Cl_2$ $C_8H_{16}S_2Cl_2$	246	0.44	0.26	0.29	0.08	0.45	—	—	—	Figure 5e
	% Organic Content in Extract		3.3	0.9	3.6	1.0	0.1				

[a] Refer to Figure 6.

[b] Based on Mass Spectral Data.

[c] Semi-quantitative estimate based on FID response.

[d] Probable number of sulfur atoms in the compound based on the M:M+2 ratio observed.

[*] Most likely molecular formula(s) based on M:M+2 ratio observed.

Table V

MAJOR COMPOUNDS IDENTIFIED IN THE CHLOROFORM EXTRACTS OF THE LIQUID HYDROLYSATE

CHROMATOGRAM PEAK NUMBER[a]	MS SCAN NUMBER[a]	COMPOUND IDENTIFIED (or tentatively identified)	MOL.[b] WT.	VAULT CONCENTRATION (μg/mL of Liquid)[c]					M:M+2 RATIO		NUMBER OF SULFUR ATOMS[d]	MASS SPECTRAL DATA
				6	7	8	9	10	EXPERIMENTAL	THEORETICAL		
1	52	1,4-Thioxane	104	32	17	—	110	10	100:7.1	100:4.7	1	Figure 3a
2	75	(2-Vinylthio)ethanol $CH_2=CH$, $HOCH_2CH_2$, S	104	—	240	—	—	—	100:6.1	100:4.7	1	Figure 3b
Not in Figure	178	*$C_4H_6S_2O$ $C_4H_6SO_2$ $C_5H_{12}SO_2$	136	—	—	2.0	4.4	—	100:13	100:91 100:5.1 100:4.9	2	Appendix 1-1
3	215	Unknown	148	24	68	19	82	48	—	—	—	Appendix 1-2
4	232	*$C_4H_{10}S_2O$ $C_4H_{10}SO_2$	138	23	—	8.9	60	40	100:13	100:9.1 100:5.1	2	Appendix 1-3
5	262	Unknown	132	2.9	—	3.3	15	5.8	—	—	—	Appendix 1-4
6	300	*$C_4H_6S_2O_2$ *$C_4H_{12}S_2O$ $C_4H_6S_2$ $C_5H_{12}SO_2$ $C_4H_{12}SO_4$	152	7.7	11	5.6	15	7.6	100:14	100:9.2 100:9.1 100:13 100:5.1 100:5.3	2	Appendix 1-5

.../2

Table V (Cont'd)

CHROMATOGRAM PEAK NUMBER[a]	MS SCAN NUMBER[a]	COMPOUND IDENTIFIED (or tentatively identified)	MOL.[b] WT.	VAULT CONCENTRATION (μg/mL of Liquid)[c]					M:M+2 RATIO		NUMBER OF SULFUR ATOMS[d]	MASS SPECTRAL DATA
				6	7	8	9	10	EXPERIMENTAL	THEORETICAL		
7	307	*$C_7H_{16}S_2$ *$C_6H_{12}S_2O$ $C_7H_{16}SO_2$ $C_6H_{12}SO_3$	164	9.4	61	—	—	—	100:16	100:9.1 100:9.2 100:5.1 100:5.2	2	Appendix 1-6
Not in Figure	313	*$C_4H_{10}S_2$ *$C_3H_6S_2O$ $C_3H_6S_2O_3$	154	—	—	5.8	16	12	100:22	100:13 100:13 100:9.4	3	Appendix 1-7
8	360	Unknown	164	15	11	7.8	27	16	m/z 166 not detected	—	—	Appendix 1-8
9	420	*$C_7H_{16}S_2$ *$C_6H_{12}S_2O$ $C_7H_{16}SO_2$ $C_6H_{12}SO_3$	164	38	130	26	63	36	100:27	100:9.1 100:9.2 100:5.1 100:5.2	3	Appendix 1-9
10	482	Unknown	152	19	11	27	11	13	m/z 154 detected at trace level	—	—	Appendix 1-10
11	531	$C_9H_{20}S_2O$ $C_8H_{16}S_2O_2$ $C_8H_{16}S_3$	208	89	110	65	160	97	m/z 210 detected at trace level	—	—	Appendix 1-11

.../3

Table V (Cont'd)

CHROMATOGRAM PEAK NUMBER[a]	MS SCAN NUMBER[a]	COMPOUND IDENTIFIED (or tentatively identified)	MOL.[b] WT.	VAULT CONCENTRATION (μg/mL of Liquid)[c]					M:M+2 RATIO		NUMBER OF SULFUR ATOMS[d]	MASS SPECTRAL DATA
				6	7	8	9	10	EXPERIMENTAL	THEORETICAL		
12	598	Unknown	—	72	82	70	79	77	—	—	—	Appendix 1-12
13	679	$C_9H_{20}S_2O$ $C_8H_{16}S_2O_2$ $C_8H_{16}S_3$	208	47	63	32	86	46	m/z 210 detected at trace level	—	—	Appendix 1-13
14	766	$C_9H_{20}S_2O$ $C_8H_{16}S_2O_2$ $C_8H_{16}S_3$	208	56	74	35	91	62	m/z 210 detected at trace level	—	—	Appendix 1-14
% Organic Content in the Extract				0.04	0.09	0.03	0.08	0.05				

a Refer to Figure 7.

b Based on Mass Spectral Data.

c Semi-quantitative estimate based on FID response.

d Probable number of sulfur atoms in the compound based on the M:M+2 ratio observed.

* Most likely molecular formula(s) based on M:M+2 ratio observed.

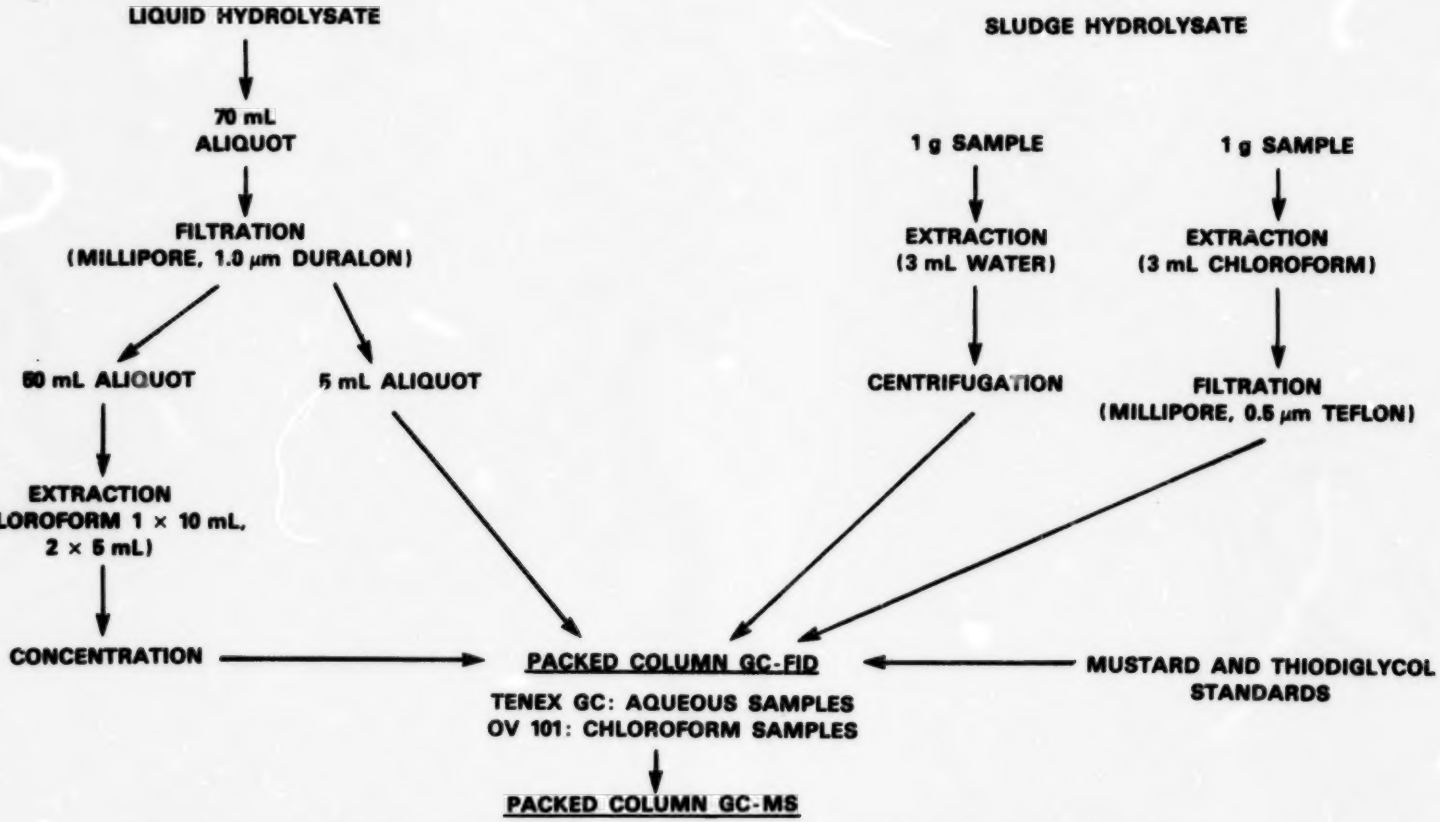


Figure 1: ANALYTICAL SCHEME USED FOR THE ANALYSIS OF DRES MUSTARD HYDROLYSATE

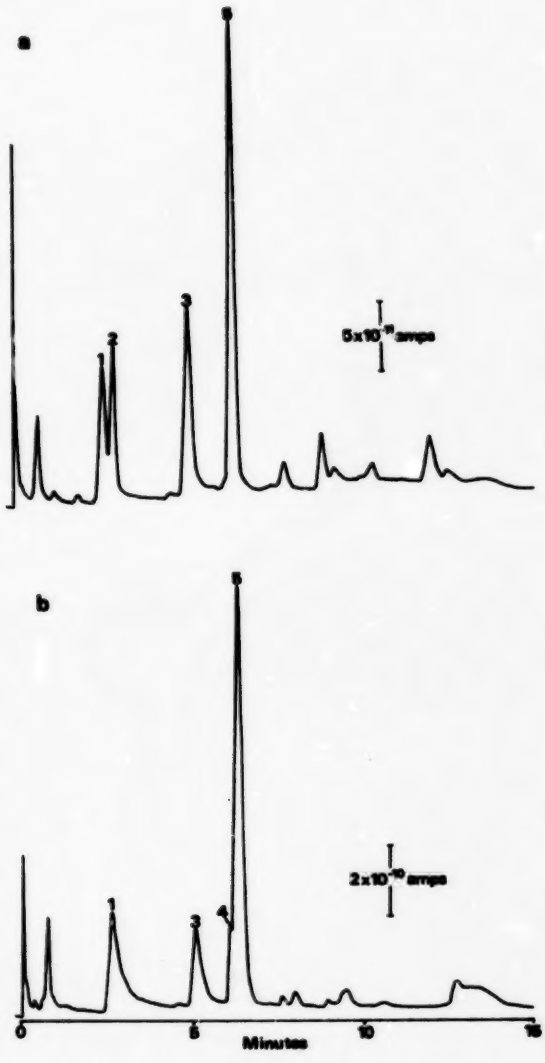
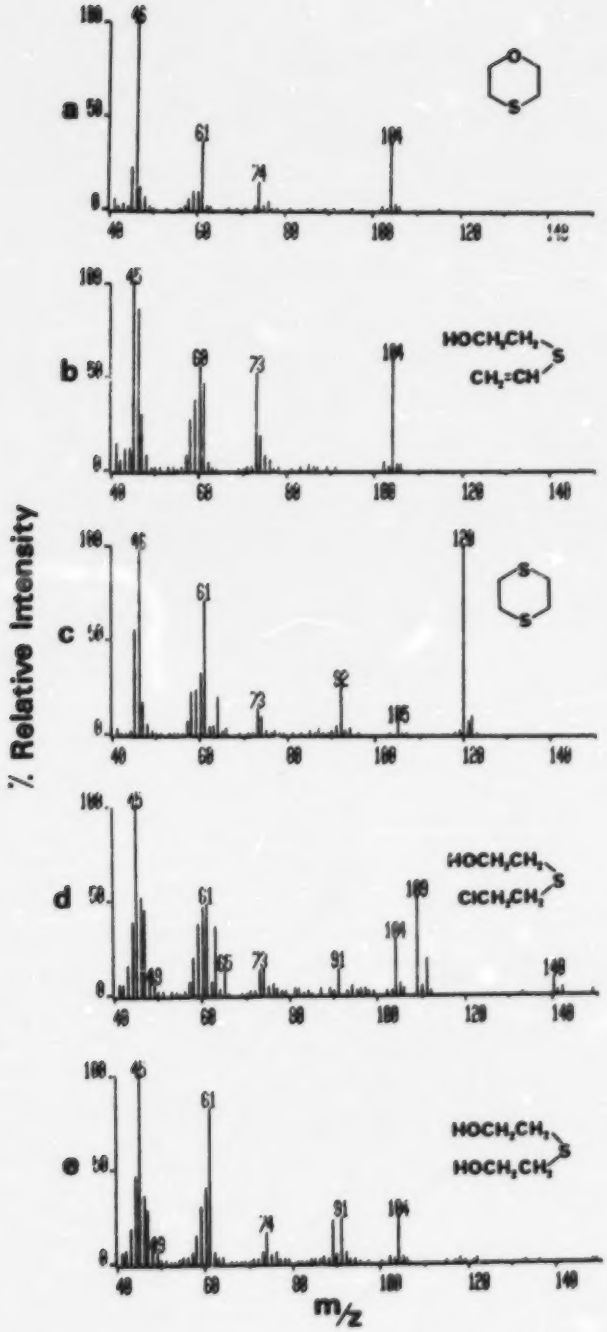


Figure 2

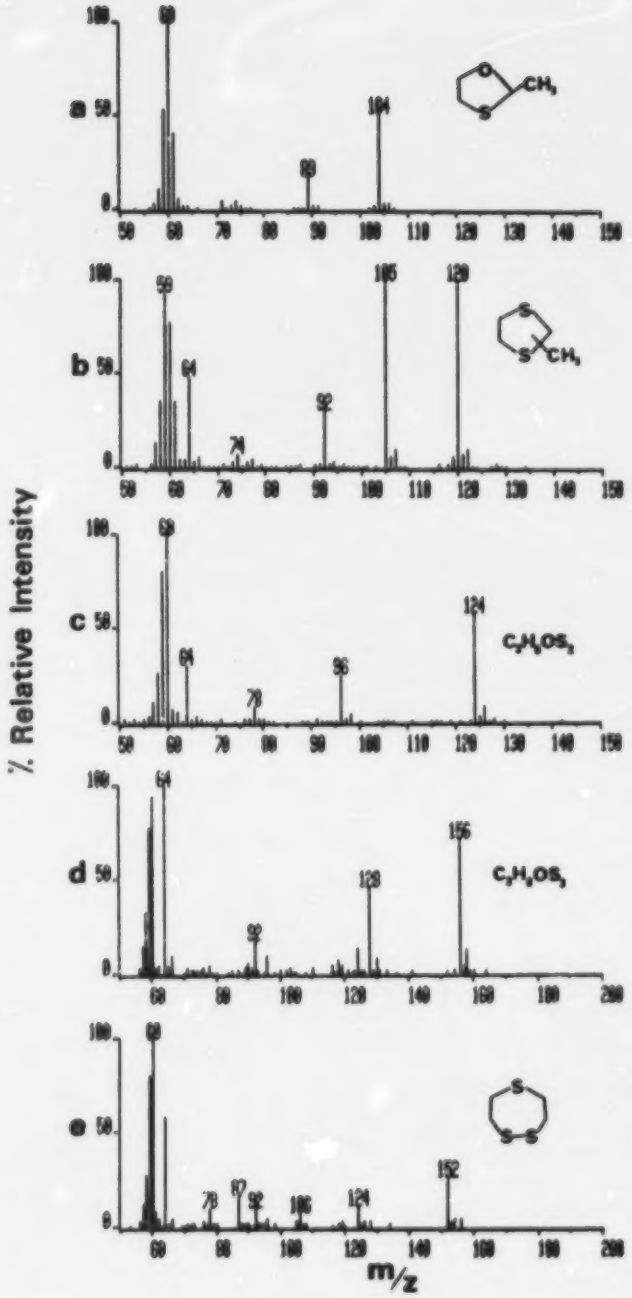
Packed Column GC-FID Chromatograms of: a) Water Extract of the Equivalent of 380 μg of Vault 7 Sludge Hydrolysate and b) 1.1 μL of Vault 9 Liquid Hydrolysate. Numbered Peaks are Identified in Table III.



m/z	Possible Ion Structure
a	
104	M^+
74	$CH_2\text{-}S\text{-}CH_2CH_2^+$
61	$H\text{-}S\text{-}CH_2CH_2^+$
46	$CH_2\text{-}S^+$
b	
104	M^+
73	$CH_2\text{-}S\text{-}CH=CH_2^+$
60	$H\text{-}S\text{-}CH=CH_2^+$
46	$CH_2\text{-}S^+$
45	$CH\text{-}S^+$
c	
120	M^+
105	$S\text{-}CH_2CH_2\text{-}S\text{-}CH^+$
92	$S\text{-}CH_2CH_2\text{-}S^+$
73	$CH_2CH_2\text{-}S\text{-}CH^+$
61	$CH_2CH_2\text{-}SH^+$
46	$CH_2\text{-}S^+$
d	
140/142	M^+
109/111	$CH_2\text{-}S\text{-}CH_2CH_2\text{-}Cl^+$
104	$HO\text{-}CH_2CH_2\text{-}S\text{-}CH=CH_2^+$
91	$HO\text{-}CH_2CH_2\text{-}S\text{-}CH_2^+$
73	$CH_2\text{-}S\text{-}CH=CH_2^+$
61	$CH_2CH_2\text{-}SH^+$
45	$CH\text{-}S^+$
e	
122	M^+
104	$HO\text{-}CH_2CH_2\text{-}S\text{-}CH=CH_2^+$
91	$HO\text{-}CH_2CH_2\text{-}S\text{-}CH_2^+$
61	$CH_2CH_2\text{-}SH^+$
45	$CH\text{-}S^+$

Figure 3

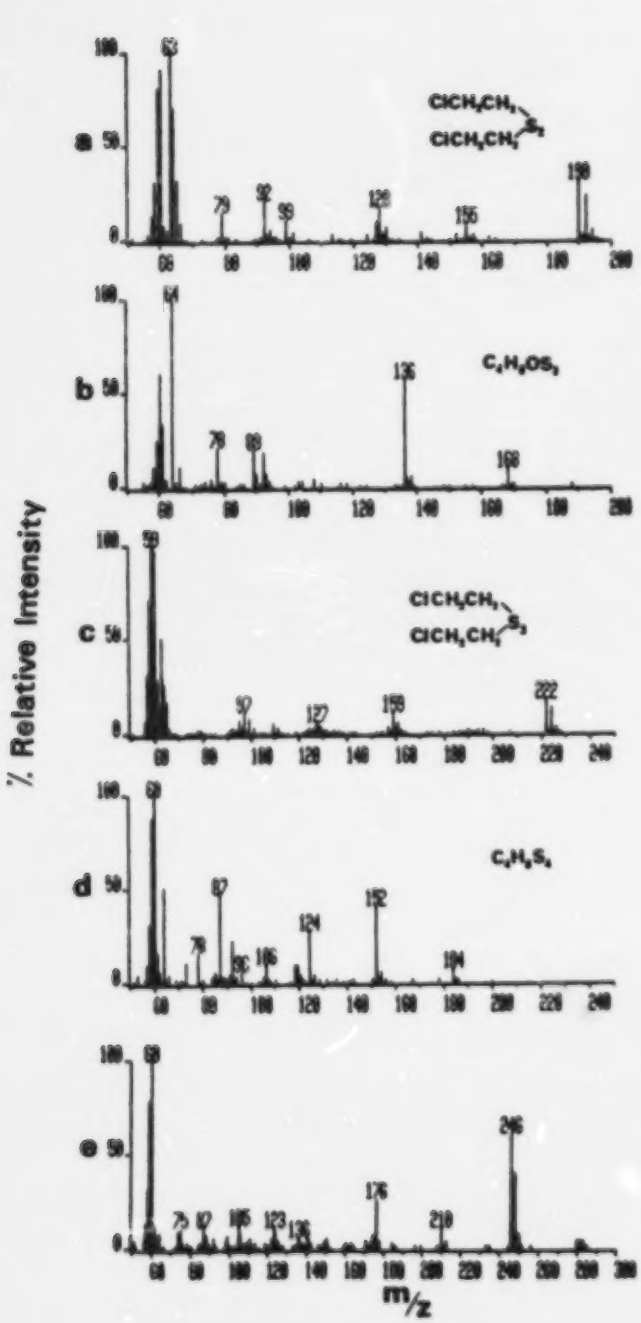
Electron-Impact Mass Spectra of: a) 1,4-Thioxane, b) (2-Vinylthio)Ethanol (tentative identification), c) 1,4-Dithiane, d) Hemisulfur Mustard and e) Thiodiglycol Identified in the Aqueous Hydrolysate Samples.



m/z	Possible Ion Structure
104	M^+
89	$(M-CH_3)^+$
60	$H-S-CH=CH_2$ $^+$
120	M^+
105	$(M-CH_3)^+$
92	$S-CH_2-CH_2-S$ $^+$
64	$S-S$ $^+$
59	$S-CH=CH_2$ $^+$
124	M^+
96	$(M-C_2H_4)^+$
78	$S-S-CH_2$ $^+$
64	$S-S$ $^+$
60	$H-S-CH=CH_2$ $^+$
156	M^+
128	$(M-C_2H_4)^+$
64	$S-S$ $^+$
60	$H-S-CH=CH_2$ $^+$
152	M^+
124	$S-CH_2-CH_2-S_2$ $^+$
106	$CH_2CH_2-S_2-CH_2$ $^+$
87	$CH_2CH_2-S-CH=CH_2$ $^+$
64	$S-S$ $^+$
60	$H-S-CH=CH_2$ $^+$

Figure 4

Electron-Impact Mass Spectra of: a) 2-Methyl-1,3-Oxathiolane (tentative identification), b) a Methyl Substituted 1,3-Dithiolane (tentative identification), c) an Unknown (probably $C_3H_6OS_2$), d) an Unknown (probably $C_3H_6OS_2$) and e) 1,2,5-Trithiepane Identified in the Chloroform Extracts of the Mustard Hydrolysate.



m/z	Possible Ion Structure
a)	
190/192/194	M^+
155/170	$CH_2CH_2-S_2-CH_2CH_2-Cl^+$
128/130	$H-S_2-CH_2CH_2-Cl^+$
92	$H-S_2-CH=CH_2^+$
79	$H-S_2-CH_2^+$
63/65	$CH_2CH_2-Cl^+$
b)	
168	M^+
136	$(M-S)^+$
92	$S-S-CH_2CH_2^+$
78	$S-S-CH_2^+$
64	$S-S^+$
c)	
222/224/226	M^+
159/161	$S_3-CH_2CH_2-Cl^+$
127/129	$S_2-CH_2CH_2-Cl^+$
97	$H-S_3^+$
59	$S-CH=CH_2^+$
d)	
184	M^+
152	$M-S^+$
124	$S_2-CH_2CH_2-S^+$
87	$CH_2CH_2-S-CH=CH_2^+$
64	$S-S^+$
60	$H-S-CH=CH_2^+$
e)	
246/248/250	M^+
210/212	$M-HCl^+$
176	$M-Cl_2^+$
123	M^{2+}
105	$CH_2-S_2-CH=CH_2^+$
87	$CH_2-CH_2-S-CH=CH_2^+$
75	$CH_2-S-CH_2CH_3^+$
60	$S-CH_2CH_2^+$

Figure 5

Electron-Impact Mass Spectra of: a) bis(2-Chloroethyl)Disulfide, b) an Unknown (probably $C_4H_8OS_2$), c) bis(2-Chloroethyl)Trisulfide, d) an Unknown (probably $C_4H_8S_4$) and e) an Unknown Containing Two Chlorine Atoms Identified in the Chloroform Extracts of the Mustard Hydrolysate.

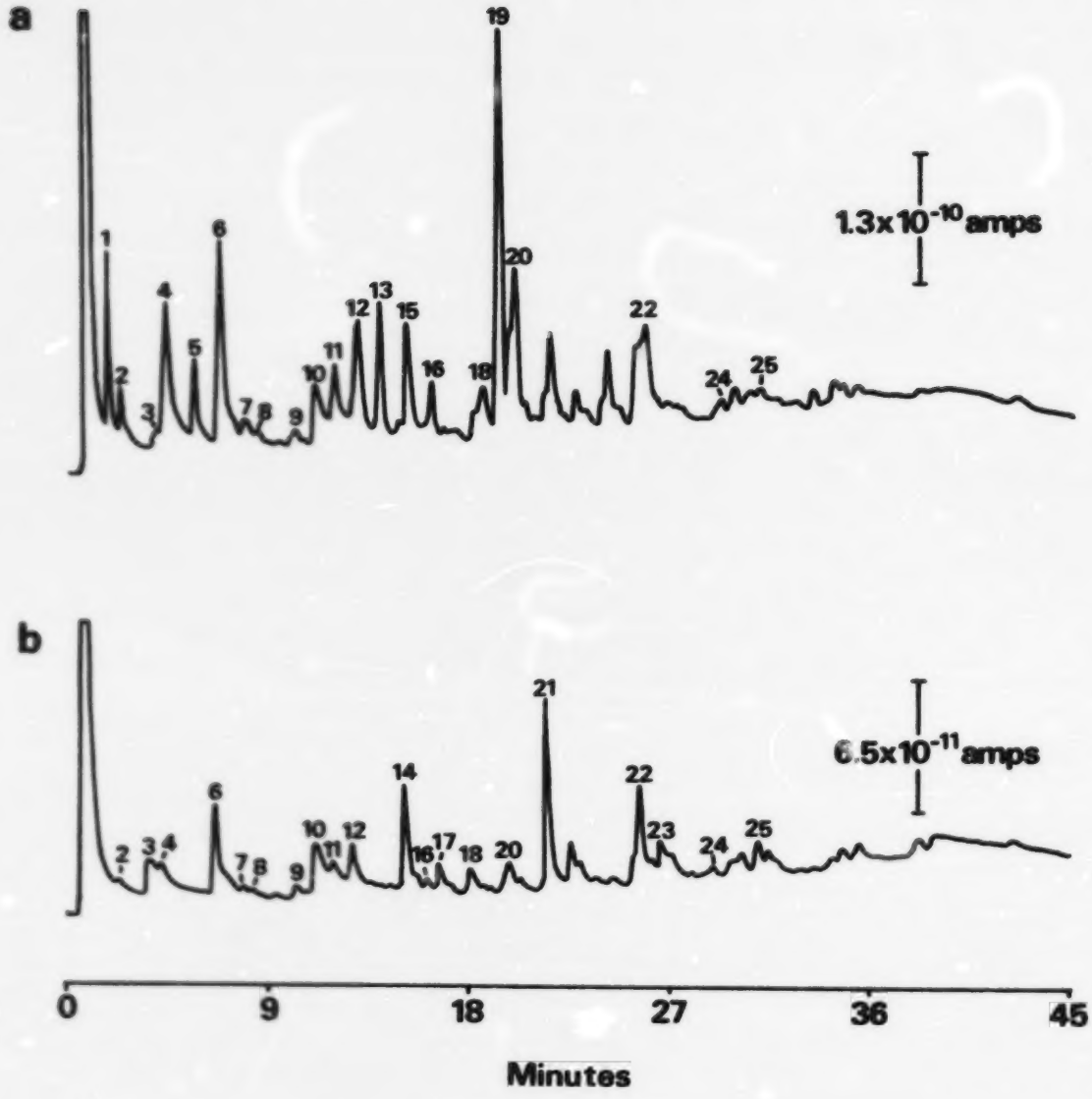


Figure 6

Packed Column GC-FID Chromatograms of the Chloroform Extracts of Two Sludge Hydrolysate Samples: a) the Equivalent of 410 μg of Vault 8 and b) the Equivalent of 390 μg of Vault 9. Numbered Peaks are Identified in Table IV.

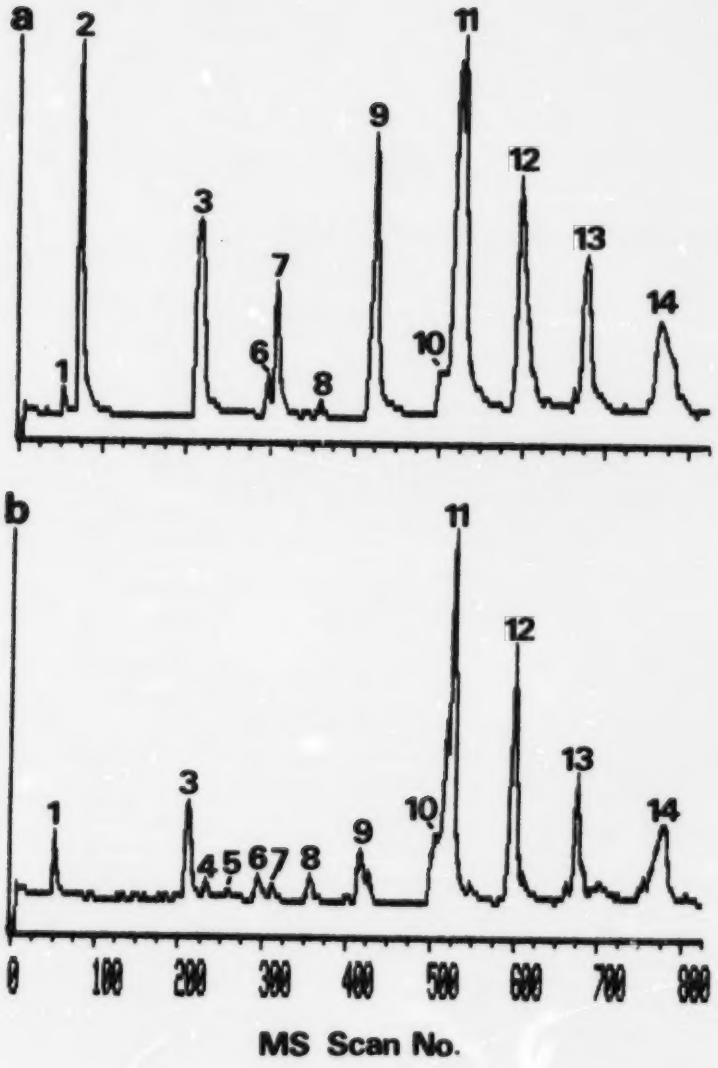


Figure 7

Packed Column GC-MS Total Ion Current Chromatograms of the Chloroform Extracts of Two Liquid Hydrolysate Samples: a) the Equivalent of 60 μL of Vault 7 and b) the Equivalent of 100 μL of Vault 6. Numbered Peaks are Identified in Table V. (One MS scan takes 3.5 sec).

Appendix 1

ELECTRON-IMPACT MASS SPECTRAL DATA FOR COMPOUNDS IDENTIFIED IN THE CHLOROFORM EXTRACTS OF THE MUSTARD HYDROLYSATE

APPENDIX NUMBER	CHROMATOGRAM PEAK NUMBER		TENTATIVE IDENTIFICATION[d]	MOL. WT.[d]	PARTIAL MASS SPECTRUM: m/z (RELATIVE INTENSITY)
	LIQUID[a] (VAULT #)[c]	SLUDGE[b] (VAULT #)[c]			
1 – 1	No Chrom. # (8,9)	—	*$C_4H_8S_2O$ $C_4H_8SO_2$ $C_5H_{12}SO_2$	136	138 (13) 137 (10) 136 (100) 108 (10) 97 (10) 93 (13) 92 (28) 89 (23) 78 (35) 64 (75) 61 (33) 60 (100) 59 (63)
1 – 2	3 (6,7,8,9,10)	—	Unknown	148	148 (1) 135 (3) 118 (4) 109 (48) 106 (23) 104 (28) 93 (10) 91 (20) 89 (50) 78 (53) 74 (38) 72 (68) 71 (100) 65 (73) 61 (100) 60 (88) 59 (83)
1 – 3	4 (6,7,8,9,10)	10 (6,7,8,9,10)	*$C_4H_{10}S_2O$ $C_4H_{10}SO_2$	138	140 (1) 138 (8) 120 (8) 105 (10) 94 (5) 91 (8) 61 (50) 60 (100) 59 (75)
1 – 4	5 (6,8,9,10)	—	Unknown	132	132 (1) 130 (1) 118 (1) 117 (1) 103 (1) 88 (25) 61 (10) 60 (100) 59 (30)
1 – 5	6 (6,7,8,9,10)	—	*$C_4H_6S_2O_2$ *$C_5H_{12}S_2O$ $C_4H_6S_2$ $C_5H_{12}SO_2$ $C_4H_{12}SO_4$	152	154 (2) 153 (3) 152 (14) 89 (5) 88 (5) 87 (100) 86 (8) 85 (8) 60 (40) 59 (58)
1 – 6	7 (6,7)	14 (6,7)	*$C_7H_{16}S_2$ *$C_4H_{12}S_2O$ $C_7H_{16}SO_2$ $C_4H_{12}SO_2$	164	166 (2) 165 (2) 164 (7) 132 (2) 120 (10) 118 (18) 105 (68) 104 (20) 91 (15) 90 (20) 87 (38) 86 (15) 85 (28) 74 (18) 73 (20) 61 (80) 60 (75) 59 (100)

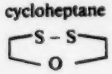
.../2

Appendix 1 (Cont'd)

APPENDIX NUMBER	CHROMATOGRAM PEAK NUMBER		TENTATIVE IDENTIFICATION[d]	MOL. WT.[d]	PARTIAL MASS SPECTRUM: m/z (RELATIVE INTENSITY)
	LIQUID[a] (VAULT #)[c]	SLUDGE[b] (VAULT #)[c]			
1 – 7	No Chrom. # (8,9,10)	—	*$C_4H_{10}S_2$ *$C_3H_6S_2O$ $C_3H_6S_2O_2$	154	156 (5) 155 (3) 154 (23) 120 (10) 92 (45) 87 (15) 79 (23) 78 (8) 76 (13) 74 (15) 64 (38) 61 (28) 60 (100) 59 (68)
1 – 8	8 (6,7,8,9,10)	—	Unknown	164	164 (2) 149 (1) 136 (8) 123 (2) 120 (2) 115 (2) 105 (10) 104 (8) 103 (3) 102 (6) 89 (13) 74 (18) 61 (53) 60 (100) 59 (73)
1 – 9	9 (6,7,8,9,10)	—	*$C_7H_{16}S_2$ *$C_6H_{12}S_2O$ $C_7H_{16}SO_2$ $C_6H_{12}SO_2$	164	166 (1) 165 (1) 164 (3) 138 (5) 120 (4) 105 (20) 104 (12) 91 (13) 76 (15) 74 (20) 73 (13) 61 (63) 60 (100) 59 (75)
1 – 10	10 (6,7,8,9,10)	—	Unknown	152	152 (1) 136 (3) 124 (2) 120 (2) 105 (45) 76 (25) 74 (20) 64 (38) 61 (33) 60 (100) 59 (80)
1 – 11	11 (6,7,8,9,10)	—	$C_9H_{20}S_2O$ $C_8H_{16}S_2O_2$ $C_8H_{16}S_2$	208	208 (2) 182 (2) 164 (4) 136 (4) 120 (10) 118 (4) 105 (25) 104 (18) 87 (15) 86 (10) 76 (15) 74 (18) 64 (15) 61 (60) 60 (100) 59 (75)
1 – 12	12 (6,7,8,9,10)	—	Unknown	—	181 (2) 164 (2) 152 (2) 138 (2) 136 (4) 134 (1) 120 (15) 118 (4) 105 (23) 92 (10) 76 (20) 74 (15) 64 (23) 61 (43) 60 (100) 59 (75)
1 – 13	13 (6,7,8,9,10)	—	$C_9H_{20}S_2O$ $C_8H_{16}S_2O_2$ $C_8H_{16}S_2$	208	208 (2) 182 (2) 164 (4) 136 (4) 120 (10) 118 (4) 105 (25) 104 (18) 87 (15) 86 (10) 76 (15) 74 (18) 64 (15) 61 (60) 60 (100) 59 (75)

.../3

Appendix 1 (Cont'd)

APPENDIX NUMBER	CHROMATOGRAM PEAK NUMBER		TENTATIVE IDENTIFICATION[d]	MOL. WT.[d]	PARTIAL MASS SPECTRUM: m/z (RELATIVE INTENSITY)
	LIQUID[a] (VAULT #)[c]	SLUDGE[b] (VAULT #)[c]			
1 – 14	14 (6,7,8,9,10)	—	$C_9H_{20}S_3O$ $C_8H_{16}S_2O_2$ $C_8H_{16}S_3$	208	208 (2) 181 (3) 164 (3) 149 (2) 136 (4) 120 (5) 118 (3) 105 (25) 104 (25) 89 (15) 87 (18) 86 (18) 76 (15) 74 (25) 64 (15) 61 (73) 60 (100) 59 (75)
1 – 15	—	7 (6,7,8)	$C_7H_{16}SO$ $C_6H_{12}SO_2$ $C_6H_{12}S_2$	148	149 (3) 148 (8) 136 (13) 105 (20) 104 (28) 103 (68) 102 (45) 89 (10) 85 (8) 76 (23) 75 (20) 74 (100) 61 (25) 60 (18) 59 (30)
1 – 16	—	8 (6,7,8)	1-Oxa-4,5-dithia-cycloheptane 	136	138 (9) 137 (6) 136 (60) 118 (45) 103 (23) 102 (15) 92 (20) 89 (25) 87 (100) 86 (28) 85 (68) 78 (13) 73 (30) 72 (45) 61 (35) 59 (50)
1 – 17	—	9 (6,7,8,9)	Unknown	140	140 (33) 133 (13) 117 (8) 111 (15) 109 (55) 108 (15) 107 (20) 106 (28) 97 (5) 93 (8) 78 (58) 75 (83) 72 (68) 71 (100) 65 (75) 63 (25)
1 – 18	—	16 (6,7,8,9)	Unknown	172	172 (18) 127 (8) 112 (8) 104 (6) 102 (6) 96 (13) 87 (100) 86 (40) 85 (20) 73 (15) 64 (13) 61 (18) 59 (40)
1 – 19	—	17 (7)	Unknown	152	152 (3) 121 (4) 120 (4) 118 (10) 104 (5) 90 (8) 61 (15) 60 (100) 59 (83)
1 – 20	—	18 (6,7,8,9)	*$C_8H_{14}S_2$ $C_8H_{14}SO_2$ $C_9H_{18}SO$	174	176 (1) 175 (1) 174 (8) 159 (2) 146 (7) 136 (6) 124 (1) 123 (1) 104 (7) 102 (3) 89 (5) 76 (10) 74 (15) 61 (28) 60 (100) 59 (73)

.../4

Appendix 1 (Cont'd)

APPENDIX NUMBER	CHROMATOGRAM PEAK NUMBER		TENTATIVE IDENTIFICATION[d]	MOL. WT.[d]	PARTIAL MASS SPECTRUM: m/z (RELATIVE INTENSITY)
	LIQUID[a] (VAULT #)[c]	SLUDGE[b] (VAULT #)[c]			
1 – 21	—	21 (7)	Unknown	—	136 (2) 134 (3) 118 (6) 105 (13) 104 (12) 103 (3) 102 (4) 90 (5) 89 (4) 88 (3) 87 (14) 86 (16) 85 (14) 84 (4) 76 (15) 61 (23) 60 (100) 59 (85)
1 – 22	—	22 (6,7,8,9)	*$C_8H_{14}S_3$ $C_8H_4S_3O_2$ $C_9H_{14}S_3O$ $C_{10}H_{22}S_2$	206	208 (10) 207 (5) 206 (43) 180 (8) 178 (25) 146 (28) 136 (13) 134 (13) 102 (100) 88 (28) 78 (10) 76 (70) 69 (13) 64 (20) 61 (25) 60 (70) 59 (53)
1 – 23	—	23 (7,9,10)	*$C_8H_{16}S_3$ $C_8H_{16}S_2O_2$ $C_9H_{16}S_2O$	208	208 (1) 206 (2) 181 (1) 178 (1) 136 (4) 120 (1) 105 (8) 104 (8) 102 (4) 89 (4) 76 (15) 74 (12) 61 (25) 60 (100) 59 (75)
1 – 24	—	24 (7,8)	$C_8H_{16}S_3$ $C_8H_{16}S_2O_2$	208	210 (13) 209 (10) 208 (55) 180 (13) 150 (10) 148 (33) 120 (8) 111 (7) 104 (43) 88 (35) 78 (10) 76 (100)

a Refer to Figure 7.

b Refer to Figure 6.

c Vault numbers where compound was identified.

d Based on Mass Spectral Data.

* Most likely molecular formula(s) based on M:M + 2 ratio observed.

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13. ABSTRACT

(U) The mustard stored at the Defence Research Establishment Suffield was disposed of by hydrolysis during the 1970's. Samples of the liquid and sludge hydrolysate were analysed by gas chromatography with flame ionization and mass spectral detection. Hydrolysis was essentially complete since only trace levels of mustard were detected. Thiodiglycol, a hydrolysis product of mustard, was found as a major component in the hydrolysate. A number of other compounds were identified (or tentatively identified) in both the liquid and sludge hydrolysate samples.

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78-270

KEY WORDS

Gas Chromatography
Mass Spectroscopy
Solvent Extraction
Chemical Agent Detection
Military Chemical Agent
Mustard Agents
Thiodiglycol
Mustard Hydrolysate

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